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STRAIN SENSING AND CHARACTERIZATION OF CNFs WRAPPED WITH POLYANILINE / POLYPYRROLE BASED POLYESTER COMPOSITES

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ABSTRACT

Flexible strain sensors are being researched excessively. The primary thoughts of maximizing the interfacial contact/ bonding between the additives and the polymer is being achieved through wrapping of carbon nanofibers with polymers and then using them as strain sensors. This causes enhancementin sensing strain of the composite. In this work, we present the novel method that can be used to wrap CNFs with polymers like Polyaniline and polypyrrole. Both polyaniline and polypyrrole have that same pendent group on a different backbone. The results related to dispersion, mechanical properties and strain sensing of this wrapped CNFs is compared to CNFs and are being reported. Hence, due to this enhanced chemical bonding a better strain sensor material is obtained. Also the studies confirmed the wrapping of polymers on the surface of CNFs.

KEYWORDS: Strain Sensor, Nanocomposites, Carbon Nanofibers, Wrapped CNFs & Polymer Wrapped CNFs

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Original Article

INTRODUCTION

In recent years, research have focused on carbon nanoparticle filled polymers because of their enhanced chemical, thermal, electrical and physical properties. Conventional metals matrix composites do not show flexibility [1,2] which is the need for wearable sensors. Furthermore, the surface modification of nanomaterials also enhances its compatibility with polymer and improves the properties one step ahead. Covalent modification (Chemisorption) and non-covalent modification (physisorption) of the surface of nanomaterials are the approaches available for the same. The later showing weaker interactions between the polymer and the CNFs compared to chemisorption. However, if in physisorption larger molecules adsorption could be achieved then it can be more significant. It is a known fact that if a good interfacial adhesion cannot be achieved, even if a very good dispersion is achieved it would not improve the properties of the materials due to weak bonding between the polymer and the additives [3]. Additives may be natural like coconut fibers [4] or synthesized like CNFs. Research have shown that the study of the curing cycle of the resin plays a role in the characteristics of the composite obtained and hence a complete knowledge of eh curing cycle is required during processing of the composite[5]. There are various treatment processes like heat treatment, Cryogenic Treatment and others for enhancing the required properties of the polymer composite [6].

CNFs also called as Stacked-cup carbon nanotubes, there are in two variants carbon fibers, Vapor Grown Carbon Fiber (VGCF) and its nano variant, Vapor Grown Carbon Nanofiber (VGCNFs). The nano variant have

drawn more attention due to high thermal, electrical and mechanical property [7]. They are typically used in materials in the form of thin film composites as they support in enhancing properties and thanks to their low cost [8]. The superior mechanical / electrical / thermal properties of carbon nanofibers (CNFs) makes it a reinforcement materials especially with polymer matrix [9]. Experimental results indicate good enhancement with respect to strength when CNFs are reinforced into the polymer matrix [10-11], but also, there are results which indicates no or limited strength enhancement [12,13].

There are two main considerations when CNFs are to be used as reinforcements which needs to be addressed. Firstly, uniform dispersion of CNFs in the matrix secondly to provide good bonding with the polymer matrix so has to enhance the stress transfer. It is this factor that the CNFs surface needs modifications before being used as reinforcement. The studies on microstructure and the diameter of the CNFs and CNTs show that CNFs has good bonding with the polymer as compared to CNTs, hence CNFs shows enhanced mechanical properties than CNTs.

Pyrograf®-III vapor-grown carbon nanofibers have very unique morphology. Nanofiber precipitate has a hollow central core which is surrounded by fiber (cylindrical) of graphite basal planes. This planes are stacked one over the other at 25 o angle along the longitudinal axis. This is why CNFs are also called stacked cup carbon nanotubes. This is what difference between CNTs and CNFs, is the exposed edge plane sites in CNFs that are more reactive and improves chemical modifications and hence provides good bonding with the polymer.

CNF's used in this study is a heat treated PR-25-XT-HHT obtained from Sigma Aldrich. This CNFs have diameters ranging 125 to 150 nm and length of 50 to 100 µm. The nanofibers are smaller in diameter than conventional carbon fibers, at the same time they are significantly larger than CNTs. In spite of this fact, they provide better mechanical properties. Generally CNFs are treated after production with an intent to change the surface state and enhance the bonding capacity with the polymer matrix.

Table 1: Properties of CNFs

Property	Value
Aldrich Product Number	719781
Pyrograf Product Number	PR-25-XT-HHT
Average Bulk Density of Product (lb/ft3)	1.2 – 3.0
*Nanofiber Density (including hollow core) (g/cm3)	1.4 - 1.6
Nanofiber Wall Density (g/cm3)	2.0 - 2.1
Average Catalyst (Iron) Content (ppm)	< 100
Average Outer Diameter, (nm)	125 - 150
Average Inner Diameter, (nm)	50-70
Average Specific Surface Area, m2/g	20 - 30
Total pore volume (cm3/g)	0.075
Average Pore Diameter(angstroms Å)	123.99

Synthesizing newer materials with improved and special properties attracts numerous applications. Polyaniline (PANI) and Polypyrrole (PPy) obtained from polymerization of aniline and pyrrole respectively. These are conducting polymers and hence are being researched for sensors applications including strain sensors. This conducting polymers combined the advantages of flexibility ease processing that of plastics and conductivity properties of metals and semiconductors. PANI is an interesting organic polymers thanks to its flexibility, lower cost, stability and a unique conduction mechanism. But has processing problems including solubility with commercially available solvents mainly due

to its stiffer backbone and the H-bonding interactions. There has been a lot of work on various synthesizing methods of PANI making it more soluble with different polymeric acids which intern improves its process ability while enhancing its electrical properties. PPy is another promising polymer which has a similar pendent group but different backbone. Basically ppy being insulator but its oxidized derivatives are good conductors of electricity. Hence, the reagent use in oxidation becomes a important parameter for its conductivity. Here, HCL is used as oxidant which makes PPY an electrically conductive material. These conductive polymers are extensively researched for its use in electronic devices, sensors and biomedical applications. PPy has been synthesized by using various techniques including electrochemical [14, 15], chemical oxidation of pyrrole monomer [16,17] in various organic solvents / aqueous media.

MATERIALS AND METHODS

The carbon nanofibers were obtained from Sigma- Aldrich (PR-25-XT-HHT). Polypyrrole was synthesized using pyrrole monomer in a polymerization technique. The chemical process was carried out in a beaker with predefined amount of distilled water with 1 molar of pyrrole monomer, HCL and Ammonium persulfate as oxidant and surfactant. Ammonium persulfate diluted with distilled water was added in the ice bath slowly. This starts the polymerization process and the same was carried out for more than 8 hrs. The fine black particles precipitated. The black powder was the filtered using What man filter paper and this was intern dried in vacuum over night at 35-40^{o} C. CNFs wrapped polypyrrole was also synthesized using pyrrole monomer. The polymerization was carried out in a beaker in a similar method while the ammonium persulfate was added in small quantities slowly, parallel to this small quantities of CNFs was added in a probe sonicator. This ensured that the CNFs were wrapped with polypyrrole. And the precipitated black power was filtered and dried in vacuum over night at 35- 40^{o}C.

Figure 1: Synthesizing of Polyaniline / Polypyrrole.

NETZSCH STA 409 (with PROTEUS software) instrument was used for weight loss measurements of all the samples which records simultaneously the mass spectra of the samples. 100 gms of the sample was placed in the crucible and the temperature ranged to about 475oC in steps of 10 k/min and held at that temperature for about 45 min. The wrapped CNFs showed a weight loss between 2 to 4 % relative to CNFs.

IGC -200 was used to estimate the surface energy of the modified CNFs. Solvents used were all spectroscopic grade. 50mg of rinsed wrapped CNFs was ground with a pestle mortar and then packed into 30cm long and 4mm dia column with retainer plugs. The same was per heated 10 100oC for a longer duration and then cooled down to about 50oC, into which solution of known physicochemical properties were injected. By finding the elution time, the dispersive surface energies have been obtained.

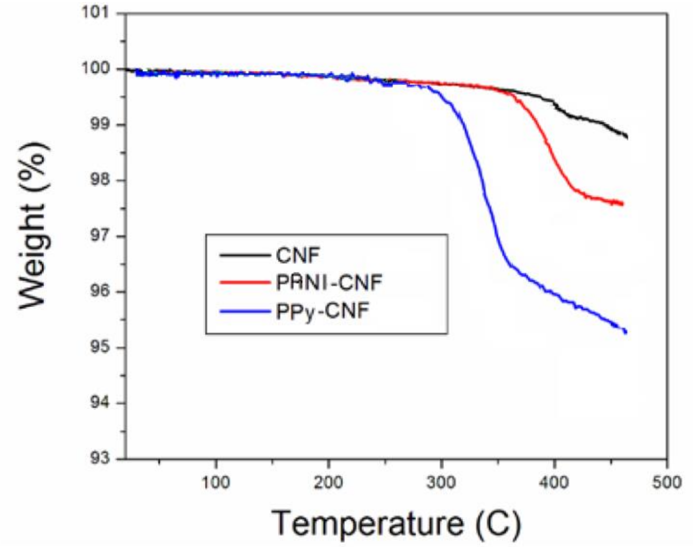

Figure 2: TGA - Weight Loss of CNF and Polymer Wrapped CNFs.

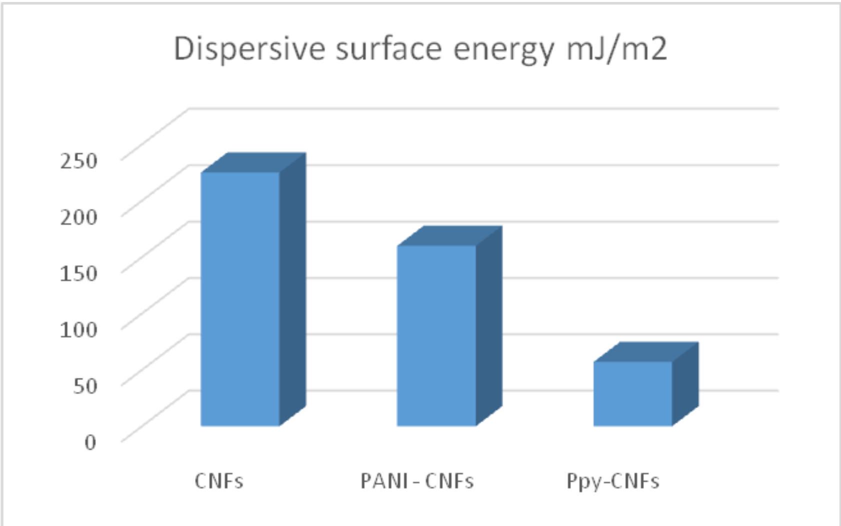

Figure 3: Dispersive Surface Energy of CNFs and Wrapped CNF.

LOAD Vs STRAIN CHARACTERISTICS

A sandwich sample using the above prepared wrapped and non-wrapped CNF with a polyester resin. These samples showed promising results for a potential strain sensing application. A cantilever setup was used to evaluate the strain sensing capabilities of the composite. As the load was applied to the end of the cantilever setup, the sensor material prepared that were attached to the bottom of the cantilever beam showed change in the resistance and the same is shown in the table 1 below. Upon loading, a clear change in resistance was observed to the corresponding change in the strain due to the loads. This showed that the materials prepared above could be used for strain sensing applications. As observed polyaniline based polyester composite showed higher resistance as compared to Wrapped CNF based polyester composite. Also, the sensitivity of wrapped CNF based polyester composite was much higher. A similar comparison can be made with Polypyrrole and CNF wrapped polypyrrole polyester composite.

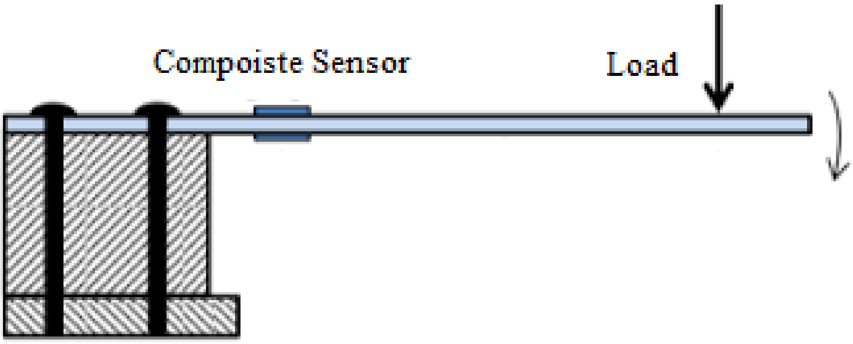

Figure 4: Strain sensing Setup

Table 2: Load and Resistance of all the Samples

Load (gms)	Resistance (KΩ)			
	Polyaniline	CNF's Wrapped Polyaniline	Polypyrrole	CNF's wrapped Polypyrrole
500	138	12	75	23
1000	136	9	73	21
1500	135	6.2	72	19.5
2000	133	4.1	71	17.5
2500	131	2.1	69	16
3000	130	0.11	68	13

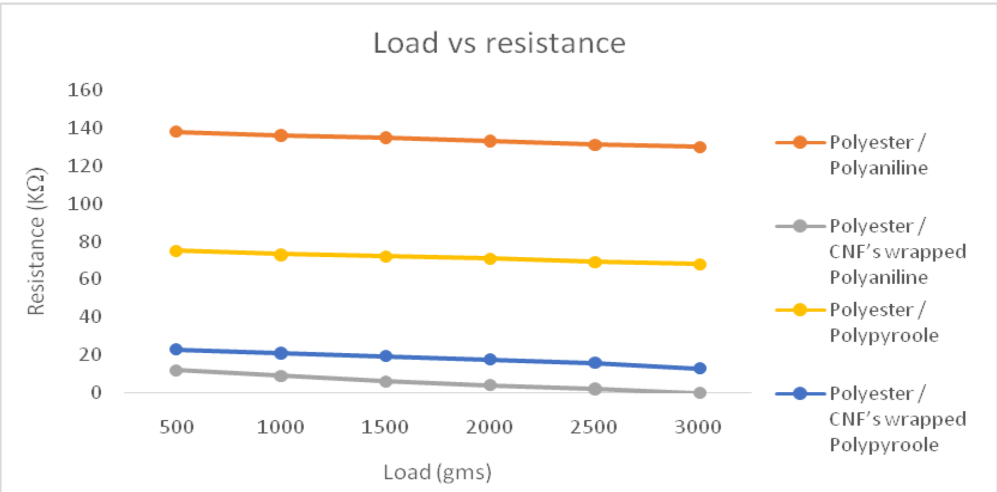

Figure 5: Load Vs Resistance Characteristics.

RESULTS AND DISCUSSIONS

It is a well-known fact that sonication plays an important part in uniform dispersion, as observed in this study, with adequate sonication, the wrapped CNFs showed less agglomeration as compared to pure CNFs when observed through SEM. TGA of the CNFs and rinsed polymer wrapped CNFs are approximately 2 % w/w for PANI and 4% w/w for PPy, this is consistent with the theories. Which suggests that there is significant amount of polymer covered on to the surface of CNFs. The decomposition remains of wrapped CNFs were compared with that of the pure polymer, there was a good correlation of the products from the neat polymer at their respective decomposition temperatures.

Inverse gas chromatography was also used to confirm the wrapping process. The dispersion surface energy of the

pure CNFs was high. Coating of CNFs resulted in a significant decrease in the dispersive surface energy as shown in the graph below. PPy wrapped CNF have shown the largest decrease in the dispersive surface energy. Hence, the use of these materials as a strain sensor is promising.

Hence a physisorption method to modify CNFs for use in composite materials specifically in sensors application has been demonstrated successfully. Sonification is effective in dispersing the pure CNFs bundles but polymer wrapped CNFs remain uniformly dispersed for a longer period of time as compared to pure CNFs. The presence of polymers was proved and loading were found between 2-4 % w/w the same was verified using IGC.

CONCLUSIONS

Wrapped CNF (polyaniline) used in polyester composite have shown higher conductivity by about 10 fold and also has enhanced the strain sensing ability by 50%. Wrapped CNF (polypyrrole) used in polyester composite have shown higher conductivity by about 3 fold and also has enhanced the strain sensing ability by 40%. The most important characteristics was the linearity the samples showed more or less good linearity.

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